

REMARKS

Applicants have amended their claims in order to further clarify the definition of various aspects of the present invention. Specifically, Applicants have amended various of the claims to recite a copper electroplating solution, instead of a copper electroplating bath comprising a solution. Applicants have further amended the claims to recite that the solution contains at least one electrolyte, at least one of the compounds represented by the general formula (I) (or at least one cyanine dye, or at least one indolium compound), and one or more polyethers, organic sulfur compounds and halide ions. In this regard, withdrawn claims 1 and 2 have been amended to be consistent with claim 3, in reciting that the solution includes one or more polyethers, organic sulfur compounds and halide ions. In light of amendments to claims 1 and 2, claims 4 and 5 have been cancelled without prejudice or disclaimer.

Independent claim 13 has been amended similarly to claim 3, to recite a copper electroplating solution containing, inter alia, at least one electrolyte, with this solution further containing one or more polyethers, organic sulfur compounds and halide ions; claim 13 has been further amended to recite that the solution further includes "an additive" selected from the group consisting of (a) cyanine dyes, (b) indolium compounds and (c) compounds represented by the general formula (I).

The remaining claims in the application, both those withdrawn and those being considered on the merits, have been amended in light of amendments to

independent claims 1-3 and 13; and, moreover, these claims have been further amended to recite materials "present" in the copper electroplating solution, rather than materials added to the copper electroplating solution.

Initially, reconsideration and withdrawal of the finality of the Office Action mailed March 25, 2004, is respectfully requested. In this regard, the Examiner's attention is respectfully directed to the claim objections set forth on pages 5-8 of the Office Action mailed March 25, 2004. These claim objections, for the most part, could have been made in connection with the original claims in the above-identified application, as considered in the Office Action mailed October 16, 2003, in the above-identified application. For example, note that the original claims recited a copper electroplating bath comprising a solution; see the objection to claim 3 bridging pages 5 and 6 of the Office Action mailed March 25, 2004.

It is respectfully submitted that by raising new objections in the Office Action mailed March 25, 2004, in connection with recitations that were not amended in the Amendment filed February 17, 2004, the Examiner could not have properly made the Office Action mailed March 25, 2004, a Final rejection. Accordingly, withdrawal of the Finality of the Office Action mailed March 25, 2004, is proper.

In any event, it is respectfully requested that the present amendments be entered. Noting the various new grounds of rejection and objections raised in the Office Action mailed March 25, 2004, it is respectfully submitted that the present amendments are clearly timely. Moreover, by clarifying the subject matter claimed in

the above-identified application, it is respectfully submitted that the present amendments clearly materially limit any issues remaining in connection with the above-identified application; and, at the least, present the claims in better form for appeal. Noting that the present amendments clarify issues, it is respectfully submitted that the present amendments do not raise any new issues, including any issue of new matter.

In view of the foregoing, it is respectfully submitted that Applicants have made the necessary showing under 37 CFR § 1.116(c); and that, accordingly, entry of the present amendments is clearly proper.

Applicants respectfully traverse the conclusion by the Examiner that claim 13 is not a generic claim, with respect to the species of claims 1-3. It is respectfully submitted that claim 13 recites, as a Markush group, the three species respectively set forth in claims 1-3, with claims 1-3 including all recitations in claim 13, as to components of the electroplating solution. It is respectfully submitted that in view of the Markush group, claim 13 reads on all three species, and thus clearly is a generic claim. The question by the Examiner as to how claim 13 can be a generic claim where it specifically recites all of the species, set forth on page 2 of the Office Action mailed March 25, 2004, is noted. It is respectfully submitted that since claim 13 reads on each of the species, e.g., individually, it clearly constitutes a generic claim. See Manual of Patent Examining Procedure, 806.04(d).

Applicants respectfully traverse the requirement by the Examiner to cancel the non-elected claims or take other appropriate action. It is respectfully submitted that in view of generic claim 13, Applicants have the right to retain the species claims in the application, to be rejoined therein upon allowance of the generic claim. Accordingly, Applicants respectfully decline to cancel the claims directed to the non-elected species claims, retaining such claims pending resolution as to allowability of generic claim 13, and respectfully traverse the requirement by the Examiner that a complete reply must include cancellation of non-elected claims or other appropriate action.

Applicants respectfully traverse the rejection of claim 13 under the first paragraph of 35 USC §112, especially insofar as this rejection is applicable to the claims as presently amended. Thus, claim 13 as presently amended recites that the solution contains "an additive" selected from the group consisting of cyanine dyes, indolium compounds and compounds represented by the specified general formula (I). As claim 13 recites "an additive", any question that claim 13 recites using a cyanine dye, an indolium compound "and" a compound represented by the general formula (I) "all together in one bath", as alleged by the Examiner, is now moot.

The objection to claims 3, 9, 13, 17 and 19, as set forth on pages 5-8 of the Office Action mailed March 25, 2004, is moot, in view of present amendments to the claims. Thus, consistent with suggestions by the Examiner, the claims have been

amended to recite a copper electroplating solution containing specified components. In addition, the other changes in wording suggested by the Examiner, with respect to claims 3, 9, 13, 17 and 19, have been made by Applicants. In this regard, the Examiner is thanked for these suggested amendments. In view of the amendments, it is respectfully submitted that the objection to the claims is moot.

Applicants respectfully traverse the rejection of claims 15-22 and 24 under the second paragraph of 35 USC §112, as set forth on pages 8-10 of the Office Action mailed March 25, 2004, particularly insofar as this rejection is applicable to the claims as presently amended. Thus, note that in the first recitation of the electroplating reaction set forth in, e.g., claims 15 and 16, claims 15 and 16 have been amended to recite "an" electroplating reaction during use of the copper electroplating solution for electroplating. In view thereof, it is respectfully submitted that there is now clear antecedent basis for the "electroplating reaction" as set forth in, e.g., claims 15 and 16. Moreover, note that claims 17 and 19 have been amended to recite "said" one or more polyethers and "said" one or more organic sulfur compounds, respectively. Clearly, the claims are sufficiently definite, to satisfy the requirements of 35 USC §112, second paragraph, with respect to the solution as claimed includes the one or more polyethers and the one or more organic sulfur compounds, respectively.

In connection with claims 22 and 24, Applicants respectfully traverse the conclusion that it is unclear as to which additive it is, that "said additive" is further

limiting. Clearly, the word "additive" is used in claim 13, providing clear antecedent basis for this term in claims 22 and 24, and therefor there is no basis for the conclusion by the Examiner that it is unclear as to which additive is being further limited in claims 22 and 24, since only one recitation of "additive" is in claim 13. Contrary to the conclusion by the Examiner, it is respectfully submitted that each of claims 22 and 24 is clear with respect to the component being further limited in claims 22 and 24.

Applicants respectfully submit that all of the claims now presented for consideration by the Examiner patentably distinguish over the teachings of the references applied by the Examiner in rejecting claims in the Office Action mailed March 25, 2004, that is, the teachings of the U.S. patents to King, et al., No. 5,174,886, to Barbieri, et al., No. 4,555,315, to Barstad, et al, No. 6,444,110, and to Landau, No. 6,261,433, and the article by Gerenrot, "Effect of the structure of carbocyanine dyes on the leveling power during the electrodeposition of copper", in Zashchita Metallov (1972), Vol. 8, No. 3, pages 338-342, under the provisions of 35 USC §103.

It is respectfully submitted that the teachings of the applied references would have neither disclosed nor would have suggested such a copper electroplating solution, or such a method of using such electroplating solution, as in the present claims, wherein the solution contains, in addition to copper ions and at least one electrolyte, at least one of the compounds represented by the general formula (I), or

an additive selected from the group consisting of cyanine dyes, indolium compounds and the compounds represented by the general formula (I), with the bath also including one or more polyethers, organic sulfur compounds and halide ions. See claim 3; note also claim 13.

In addition, it is respectfully submitted that these references as applied by the Examiner would have neither disclosed nor have suggested such copper electroplating solution as in the present claims, having features as discussed previously, and further including (but not limited to) wherein the at least one of the compounds of the general formula (I) is added in a concentration of 1-15 mg/L (see claim 9); and/or wherein one or more polyethers (see claims 17 and 18) or one or more organic sulfur compounds (see claims 19 and 20), is included in the electroplating solution.

Furthermore, it is respectfully submitted that these references as applied by the Examiner would have neither disclosed nor would have suggested such process for producing a semiconductor integrated circuit device, using the copper electroplating solution, or such copper electroplating solution, as in the present claims, having features as discussed previously in connection with independent claims 3 and 13, and, moreover, wherein the additive (compounds represented by the general formula (I)) suppresses the electroplating reaction occurring during the electroplating procedure and are consumed as the electroplating reaction proceeds, with a diffusion rate thereof being lower than a rate of reaction thereof during use of

the copper electroplating solution (see claims 15 and 16; note also claims 21 and 22); and/or wherein the concentration of the compounds represented by the general formula (I), or of the additive, in the copper electroplating solution, at the bottoms of the features, during the process, is less than that at the top of the features (see claims 23 and 24).

The present invention is directed to a copper electroplating solution, in particular a copper electroplating solution especially useful for depositing copper in, and filling, fine openings or grooves in insulating layers, used, for example, in manufacturing semiconductor integrated circuit devices having multi-layer interconnections.

Recently, copper has been used for interconnections of large-scale integrated circuits, replacing aluminum and alloys thereof, due to, e.g., relatively low resistance of the copper. When using copper, it is difficult to pattern by dry etching, to form fine patterns, because copper does not produce a compound having a high vapor pressure. Accordingly, there has been employed a technique, called a Damascene technique, wherein trenches and vias are formed in insulating layers and filled with copper, the copper being isolated in the trenches and vias by, e.g., chemical mechanical polishing. While various techniques for filling the trenches and vias have been proposed, electroplating is the most promising as a method for filling the trenches and vias. Note, for example, the paragraph bridging pages 2 and 3 of Applicants' specification.

While various techniques have been studied to fill trenches and vias with metals by electroplating, each of the proposed techniques has a problem, as discussed on pages 3 and 4 of Applicants' specification. These problems include, in particular, wherein voids and seams occur in the trenches and vias, particularly those having a high aspect ratio; and there is a particular need for a technique which allows such fine features to be completely filled.

Against this background, Applicants provide a technique wherein a completely filled feature (e.g., trench or via) can be provided, without generating voids and seams, even where such feature has a high aspect ratio; and, moreover, wherein uniformity in film thickness and film flatness is achieved. Applicants have found that by including in the copper electroplating solution, in addition to copper ions and at least one electrolyte, at least one of the compounds represented by general formula (I) in claim 3 (or an additive selected from the group consisting of cyanine dyes, indolium compounds, and the compounds represented by general formula (I)), and together with at least one selected from the group of polyether, organic sulfur compound and halide ions, objectives according the present invention are achieved. That is, the electroplated copper fills the inside of the feature, without voids or seams; and, moreover, the deposited structure has a uniform film thickness and film flatness on, e.g., the wafer upon which the copper is electrodeposited, facilitating polishing of the plated copper.

In connection with advantages achieved by the present invention, note, for

example, Tables 1 and 2, respectively on pages 17 and 21 of Applicants' specification. Note that Sample Numbers 1, 2 and 9 do not contain the additional component selected from the group consisting of polyethers, organic sulfur compounds and halide ions, while Sample Numbers 3-8 contain such additional component. As can be seen, for example, in Table 2, uniformity is much better in connection with Sample Numbers 3-8. This evidence in Applicants' specification must be considered in determining unobviousness. See *In re DeBlauwe*, 222 USPQ 191 (CAFC 1984). This evidence further supports the conclusion of unobviousness of the presently claimed subject matter.

While Applicants rely on evidence in their specification showing unexpectedly better results, the Examiner has not commented on this evidence, in the Office Action mailed March 25, 2004. Such failure to comment on evidence properly before the Examiner is clearly improper. It is respectfully submitted that, when properly taken into account, this evidence further supports the conclusion of unobviousness of the presently claimed subject matter.

King, et al. discloses a high-throw aqueous acidic bath for the electrodeposition of copper containing additives to produce printed circuit boards having plated through-holes, the plating bath comprising an aqueous solution of (A) copper sulfate, (B) sulfuric acid, (C) chloride ion, (D) a carrier, (E) a brightener and (F) an alkali metal salt, with pH of the plating bath being not greater than 2, a concentration of the chloride ion, and mole ratio of copper sulfate to sulfuric acid, in

the bath, being defined. See column 2, lines 18-36. Also disclosed is a process of using this bath for copper plating. See column 4, lines 17-37. See also column 3, lines 4-6.

It is respectfully submitted that King, et al. is concerned with providing a high-throw acid copper plating solution, not a copper plating solution for plating high aspect ratio features. It is respectfully submitted that this reference does not disclose nor would have suggested, such a plating solution, or use thereof, as in the present invention, including, inter alia, both the additive (in particular, (a) at least one of the compounds represented by the general formula (I) and (b) one or more polyethers, organic sulfur compounds and halide ions), as in the present claims, and advantages achieved thereby.

It is respectfully submitted that this reference also would have neither disclosed nor would have suggested the other features of the present invention, including, inter alia, filling the inside of the features with copper (note, for example, claims 12 and 20); and/or wherein the additive (or the compound represented by the general formula (I)) suppresses an electroplating reaction during use of the copper plating solution for electroplating and is consumed as the electroplating reaction proceeds, with a diffusion rate thereof being lower than a rate of reaction thereof during use of the copper electroplating solution for electroplating (note, e.g., claims 15 and 16; note also claims 21 and 22).

Comments by the Examiner on page 13, lines 5-13 of the Office Action mailed March 25, 2004, are noted. It is respectfully submitted that the claim recitations constitute specific recitations in connection with the materials used and in connection with the processing, which must be considered in determining patentability. That is, for example, claim 15 defines a property of the additive, which can compositionally distinguish the bath from prior art. It is respectfully submitted that this property of the additive must be considered in determining patentability.

The contention by the Examiner that a newly discovered use or function of components does not necessarily mean the system is unobvious "since this use or function may be inherent in the prior art" is noted. It is respectfully submitted that for a use or function to be inherent, it must occur throughout all teachings of the applied reference. It is respectfully submitted that the Examiner has not established inherency, in the electroplating bath and process disclosed or suggested by the prior art, of claimed features of the present invention.

It is respectfully submitted that the additional teachings of Gerenrot would not have rectified the deficiencies of King, et al., such that the presently claimed invention as a whole would have been obvious to one of ordinary skill in the art.

Gerenrot discloses the results of a study of the relation between the structure of polymethine dyes and their leveling power during copper electrodeposition from acid solutions. The article discloses that the greatest leveling power was obtained

with carbocyanines with the highest basicity. Note the English Abstract of this article.

Initially, it is respectfully submitted that one of ordinary skill in the art concerned with in King, et al., would not have looked to the teachings of Gerenrot. Thus, note that King, et al. is concerned with high-throw acid copper plating baths, for plating through-holes; on the other hand, Gerenrot is concerned with providing solutions having leveling power. It is respectfully submitted that one of ordinary skill in the art concerned with in King et al., looking to high-throw plating baths, would not have looked to baths with leveling power as in Gerenrot. It is respectfully submitted that only through the disclosure of the present invention would one of ordinary skill in the art concerned with in King, et al. have looked to materials as in Gerenrot. Of course, such hindsight use of Applicants' disclosure is improper under 35 USC §103.

Even if properly combinable, it is respectfully submitted that the combined teachings of King, et al. and of Gerenrot would have neither taught nor would have suggested the present invention, including advantages thereof in improved plating in high aspect ratio features; and, in particular, the subject matter of, e.g., claims 15, 16, 21 and 22; or the processing as in claims 23 and 24.

It is respectfully submitted that the additional teachings of Barbieri, et al. and Barstad, et al. would not have rectified the deficiencies of the teachings of King, et al. and of Gerenrot, such that the presently claimed invention as a whole would have been obvious to one of ordinary skill in the art.

Barbieri, et al. discloses an electrolyte composition and process for electrodepositing copper, the composition including an additive system comprising controlled selected relative amounts of (a) a bath soluble polyether compound; (b) a bath soluble organic divalent sulfur compound; (c) a bath soluble adduct of a tertiary alkyl amine with polyepichlorohydrin; and (d) a bath soluble reaction product of polyethyleneimine and an alkylating agent which will alkylate the nitrogen on the polyethyleneimine to produce a quaternary nitrogen, the alkylating agent being selected from a specified group. Note the paragraph bridging columns 1 and 2 of this patent. Note also column 2, lines 38-43; column 3, lines 3-6 and 49-55; and column 4, lines 33-40.

Barstad, et al. discloses copper electroplating solutions and methods for using such solutions, with the solutions including a copper salt, an electrolyte preferably an acidic aqueous solution such as a sulfuric acid solution with a chloride or other halide ion source and one or more brightener agents in enhanced concentrations, and preferably a suppressor agent. See column 3, lines 41-46. Note also column 2, lines 44-57, and the paragraph bridging columns 2 and 3. This patent discloses that through use of a surfactant-type suppressor agent, in combination with elevated brightener concentrations, effective bottom-fill copper plating of a microvia or other aperture without defects such as inclusions or voids can result. See column 3, lines 20-26. Note also column 6, lines 23-38 for specific suppressor agents.

Even assuming, arguendo, that the teachings of Barbieri, et al. and Barstad, et al. were properly combinable with the teachings of King, et al. and Gerenrot, such combined teachings would have neither disclosed nor would have suggested the presently claimed subject matter, including the copper electroplating solution containing, inter alia, the recited additive in claim 13 (or at least one of the compounds represented by the general formula (I) in claim 3) together with one or more polyethers, organic sulfur compounds and halide ions, achieving advantages of the present invention as discussed in the foregoing.

As for the process claims, Applicants respectfully traverse the conclusion by the Examiner that the subject matter of these claims would have been obvious within the meaning of 35 USC §103, as alleged by the Examiner in Items IV-VII on pages 15-20 of the Office Action mailed March 25, 2004.

Landau discloses an apparatus and a method for electroplating a metal layer onto a substrate, the apparatus being described most generally in the paragraph bridging columns 4 and 5 of this patent. As for the chemistry of the electrodeposition, note column 17, lines 41-44 and 57-59; and column 18, lines 12-15, of this patent. As for operating conditions as described in this patent, see columns 15-17 therein.

Gerenrot has been previously discussed.

Even assuming, arguendo, that the teachings of Landau, et al. and of Gerenrot were properly combinable, such combined teachings would have neither

disclosed nor would have suggested the presently claimed process, including use of a copper electroplating solution having, in addition to copper ions and at least one electrolyte, both the specified additive (including the compounds represented by the general formula (I) in claims 3 and 13) and one or more polyethers, organic sulfur compounds and halide ions, and advantages thereof essentially in connection with plating high aspect ratio features; and wherein the additive (at least one of the compounds represented by the general formula (I)) suppresses an electroplating reaction during the process and is consumed as the electroplating reaction proceeds, and has a lower diffusion rate than a rate of the reaction thereof during the process (note claims 21 and 22); and/or wherein during the process concentrations of the additive (at least one of the compounds represented by the general formula (I)) in the electroplating bath at the bottoms of the features is less than that at the top of the features.


In view of all of the foregoing, reconsideration and withdrawal of the finality of the Office Action mailed March 25, 2004, with resulting entry of the present amendments, and reconsideration and allowance of all claims then in the application, are respectfully requested. In any event, entry of the present amendments, and reconsideration and allowance of all claims then in the application, are respectfully requested.

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Respectfully submitted,


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